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(54) **Pyrotechnic sheet material**

(57) The invention provides pyrotechnic sheet material comprising a substrate of oxidizing polymeric film, for example a film of halogenopolymer, having a coating layer of oxidizable material, for example magnesium, on at least part of its surface, the substrate and the oxidizable material being conjointly capable of reacting together on ignition. Overlying at least a portion of the surface area of the substrate and/or the oxidizable material is a layer of gas-generating deflagrating material, for example a nitrocellulose propellant, which may for example be an adherent layer or a separate layer such as a co-rolled layer.

The deflagrating material enhances the flame transmission properties and igniting ability of igniferous booster charges comprising the pyrotechnic sheet material. It also protects the oxidizable material from atmospheric oxidization.

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Description

This invention relates to gas-generating pyrotechnic sheet material which is especially useful in igniferous booster charges (hereafter termed ignition lements or igniters) for prop llant compositions. In vehicl occupant restraint safety systems the material may be used advantageously in ignition elements for gas-generating compositions for gas-bag ("air bag") inflation and heating elements for heating stored gas in hybrid inflators. The invention also relates to the method of manufacturing said pyrotechnic sheet material.

Pyrotechnic sheet material consisting of one or more substrate layers of oxidizing polymeric film having a layer of oxidizable material, preferably metal, on at least a portion of at least one surface of the, or each, substrate layer, the polymeric film and the oxidizable material being conjointly capable of reacting together exothermically on ignition, has been described in PCT International Publications Nos WO 90/10611 and WO 90/10724. Improved pyrotechnic sheet material having enhanced burning rate has been described in United Kingdom patent specification No. GB 2,282,136A.

The use of the aforesaid pyrotechnic sheet material to ignite a gas-generating propellant charge for air bag inflation has been described in European patent publication no. 505024.

The preferred oxidizing polymeric film is halogenated film such as polytetrafluoroethylene containing little if any hydrogen and the preferred oxidizable material of the aforedescribed pyrotechnic sheet material comprises a metal selected from the group consisting of lithium, sodium, magnesium, beryllium, calcium, strontium, barium, aluminium, titanium, zirconium, and alloys of any one or more thereof, the most preferred metal being magnesium. Advantageously the metal is vapour-deposited on the film by known methods, the amount of metal being preferably substantially stoichiometric at the location of the film underlying the metal. On ignition this pyrotechnic sheet material produces substantially only solid products, any gases such as metal fluoride produced in the combustion zone instantaneously condensing to solid form. Such gasless material is advantageous in certain applications where blast effects must be avoided, but in applications where the material is primarily required to propagate flame to a further charge of combustible material the absence of gaseous products can be a disadvantage.

We have now found that the ease of ignition and flame transmission properties of the aforedescribed pyrotechnic sheet material can be enhanced by providing the sheet with a contacting layer of gas-generating deflagrating material. The resulting pyrotechnic sheet has the fast burning rate of the original material and also produces gas which rapidly travels to, and penetrates, any ignitable gas-generating main charge in contact with the sheet material, thereby accelerating the ignition of the main charge. In addition to enhancing the flame transmission capability, the layer of deflagrating material can also act as a protective barrier mat rial to prevent r retard oxidation of a layer of oxidizable material such as magnesium which oxidizes at a significant rate under normal atmospheric conditions. When enhanced ease of ignition only is required this effect can be achieved by the application of the deflagration material over a small portion of the pyrotechnic sheet material adjacent to an ignition point and the amount of deflagrating material need not be sufficient to produce a significant amount of gaseous products on combustion.

Thus, in accordance with this invention pyrotechnic sheet material comprises a substrate of oxidizing material; a coating layer of oxidizable material on at least a portion of at least one surface of said substrate, the said substrate and the said layer of oxidizable material being conjointly capable of reacting together exothermically on ignition; and a layer of gas-generating deflagrating material overlying at least a portion of the surface area of the substrate and/or the layer of oxidizable material, said deflagrating material being in ignition transmission relationship with said substrate and oxidizable material. Deflagrating material in this context refers to material capable of sustained rapid burning without reaction with further oxidizing or reducing material.

The gas-generating deflagrating material may be applied as an adhering layer to the substrate and/or the layer of oxidizable material or it may be provided as a separate layer over a free surface of the substrate and/or the oxidizable material, for example as a co-rolled sheet. The substrate may advantageously be coated on both sides with oxidizable material and at least a portion of at least one of the layers of oxidizable material may advantageously be covered with a layer of gas-generating deflagrating material.

The gas-generating deflagrating material may, for example, comprise any gas-generating propellant material. A nitrocellulose based propellant is advantageous and convenient and may, for example, be applied to the film or oxidizable material as a separate sheet in laminar pyrotechnic sheet material of the invention, or as a solution in a solvent, for example acetone, which is subsequently removed to leave an adherent layer of nitrocellulose propellant material on the film or oxidizable material. Other gas-generating propellant materials which may be used include deflagrating materials such as black powder, sodium azide/oxidizer compositions, potassium perchlorate/aluminium compositions or other solid pyrotechnic gas-generating composition. These may be applied over the coated substrate as a solution or dispersion in a carrier liquid which can be removed, or in a curable liquid polymer or in a polymer solution, such as polymethyltrifluoroethylene in acetone or polyvinylacetate in water, from which the solvent can subsequently be removed.

The layer of gas-generating deflagrating material is conveniently from 3-100 microns thick and preferably from 10-40 microns thick.

The preferred oxidizing substrate comprises polymeric film preferably containing atoms chemically bound

therein selected from the group consisting of halogens (especially fluorine), oxygen, sulphur, nitrogen and phosphorous. One preferred film substrate comprises fluoropolymer such as polytetrafluoroethylene (PTFE) which produces a high energy pyrotechnic sheet, but other suitable polymeric films include those comprising polychlorotrifluoroethylene, polyhexafluoropropylene, copolymers of trifluoroethylene and hexafluoropropylene, copolymers of trifluoroethylene and tetrafluoroethylene, copolymers of hexafluoropropylene and tetrafluoroethylene,
copolymers of hexafluoropropylene and vinylidene fluoride,
copolymers of tetrafluoroethylene and partially fluorinated propylene, copolymers of chlorotrifluoroethylene and vinylidene fluoride, homopolymers of partially fluorinated propylene, copolymers of partially fluorinated propylene and vinylidene fluoride, trichloroethylene homopolymers, copolymers of trichloroethylene and vinylidene fluoride, mixtures of two or more of such polymers or mixtures of any one or more of such polymers with PTFE.

The polymeric film may optionally be a porous film, the pores advantageously occupying 6-95% of the film volume (i.e. porosity of 6-95%). Preferably the pores are interconnecting vapour-permeable pores having at least part of the oxidizable material vapour-deposited therein. Pyrotechnic sheet material comprising such porous film generally has faster burning rates than that containing only solid polymeric film.

A preferred pyrotechnic sheet of the invention has discontinuous portions in the oxidizing substrate and/or the layer of oxidizable material, preferably in the oxidizable material, these portions having flame-permeable apertures through which the interface between the oxidising substrate and the oxidizable material is exposed as described in United Kingdom patent specification no.GB 2,282,136A which is incorporated herein by reference. Such exposure of portions of the interface enhances the ease of ignition and rate of combustion of the pyrotechnic sheet. In an especially preferred pyrotechnic sheet the substrate and the oxidizable material are permanently deformable and have different strains for rupture value thereby enabling one of the materials to be ruptured by stretching to expose flame-permeable apertures at the interface. The stretching may advantageously be effected by stamping protrusions (embossing) on the contacting substrate and layer of oxidizable material, the protrusions subsequently serving as spacer elements to enhance the rate of combustion of the pyrotechnic sheet material.

The oxidizable material may advantageously comprise metal selected from the group consisting of lithium, sodium, magnesium, beryllium, calcium, strontium, barium, aluminium, titanium, zirconium and alloys thereof, which metal may be advantageously be vapour-deposited on the substrate. A metal layer is especially advantageous as it significantly enhances the dimensional stability of the pyrotechnic sheet and is easily ruptured.

A most preferred metal for high heat generation is magnesium or an alloy thereof preferably coated on to a substrate film comprising fluoropolymer. Preferably the ratio of metal to the substrat of oxidizing polymeric film is substantially stoichiometric or there is a small excess of metal at the location of the film underlying the metal. The reaction between PTFE and magnesium can be represented empirically as

$$(C_2F_4)n - 2nMg \rightarrow 2nMgF_2 + 2nC$$

This reaction releases 5.98 megajoules/kilogram of reactant pyrotechnic material.

The rate of energy release on ignition varies inversely with the thickness and directly with the porosity of the pyrotechnic sheet material and, accordingly, the thickness and porosity will be chosen to attain the desired energy release. Thus the preferred polymeric film will generally have an areal mass of 10 to 150g/m^2, typically 25-75g/m^2 and the total amount of the oxidizable material will be equivalent to a laminar thickness of 2 to 30 microns, typically 4 to 15 microns.

A typical pyrotechnic sheet comprises a film of halogenopolymer 3 to 50 microns, (preferably 10 - 30 microns) thick having on each side a vapour-deposited layer of magnesium 2 to 40 microns (preferably 4 - 15 microns) thick, each magnesium layer being overlaid with a contacting layer of gas-generating deflagrating material 10 - 40 microns thick.

The invention also includes a method of manufacturing a pyrotechnic sheet material which comprises depositing a layer of oxidizable material on at least a portion of at least one surface of a substrate of oxidizing material, the substrate and the oxidizable material being conjointly capable of reacting together exothermically on ignition, and applying to at least a portion of the surface of the oxidizable material and/or the substrate an overlying layer of gas-generating deflagrating material in ignition transmission relationship with said substrate and oxidizable material.

Preferably the oxidizable material is vapour-deposited at low pressure on the polymer substrate by direct evaporation or magnetron sputtering.

The invention is further described by way of example only with reference to the accompanying drawing which is a diagrammatic perspective, part-sectional view of pyrotechnic sheet material of the invention.

Referring to the drawing, pyrotechnic sheet material designated generally by the number 10 consists of a substrate 11 of oxidizing polymeric film, for example of polytetrafluoroethylene, coated on each side with a vapour-deposited layer of oxidizable metal for example magnesium 12. Each layer of oxidizable metal is coated with a layer of gas-generating deflagrating material 13.

The manufacture of the pyrotechnic sheet material of the invention is further described in the following specific Examples wherein parts and percentages are given by weight.

Example 1

A 25 micron thick solid sheet of PTFE was coated on each side with an 8.5 micron thick vapour-deposited layer of magnesium (approximately stoichiometric proportions). Th coated sheet was embossed with regular rows of dimples by passing the sheet between a patterned metal roll and a plain rubber roll. The dimples were spaced at 3mm centres in each direction and each dimple was approximately 0.75mm square at the base, 0.5mm square at the top, and 0.25mm high. The upper layer of magnesium was thereby ruptured around the periphery of the top of the dimples to expose the oxidizing polymeric film at the magnesium/PTFE upper interface, the width of the exposed areas being up to 10 microns.

A sample portion of the embossed sheet having an area of 164 cm^2 was coated with a solution in acetone of nitrocellulose, having a nitrogen content of 12.2%, and the acetone was evaporated off to leave a continuous contacting film of nitrocellulose over the layers of magnesium.

The sample was rolled into a helically wound charge assembly by winding around a central tubular phenolic resin former having an internal diameter of 6mm and 6mm wall thickness. Three longitudinal slits extending to within 10mm from each end of the charge were cut through the spiral section of the pyrotechnic sheet. The assembled charge was ignited by a squib in a combustion test vessel (ballistic bomb) having a volume of 35cc.

The pressure in the vessel alter ignition was recorded. A sample coated with 0.1g nitrocellulose gave a maximum pressure of 22.1MPa in 2.02 milliseconds and a sample coated with 0.21g nitrocellulose gave a maximum pressure of 27.9MPa after 1.84 milliseconds. In a comparative test a sample without a nitrocellulose coating gave a maximum pressure of 20MPa after 2.03 milliseconds.

These results clearly demonstrate the improved pressure (gas production) obtained with the nitrocellulose coated material.

Example 2

A pyrotechnic sheet comprising 25 micron thick PTFE film coated on each side with an 8.5 micron thick vapour-deposited layer of magnesium was prepared and embossed as described in Example 1. A 10.61g sample of the embossed sheet was cut to the shape of a trapesium with opposite parallel sides having respective lengths of 150mm and 118mm and a length of 0.8 metres between opposite equal sides. The sample was coated on each side with a slurry containing 4 parts sodium azide, 0.065 parts carbon black, 1.81 parts vinylidene fluoride/hexafluoropropylene copolymer (binder and oxidizer for the sodium azide) available under the registered trade mark VITON and 8.37 parts ethyl acetate. The ethyl acetate was r moved by evaporation leaving 3.09g of residual coating material. The sample was wound around a 12mm diameter tubular phenolic resin former with the shorter parallel edge on the inside and ins rted into a 28mm diameter x 11.7mm long thin steel tube leaving about 15mm at each end of the sample protruding beyond the steel tube. Each protruding end was 'petalled' by making 6 equally spaced longitudinal cuts around the circumference, each cut extending to 1cm from the end for a length of 15mm.

Two such wound samples here placed in proximity in a ballistic bomb having a volume of 7100 cc and ignited simultaneously at the end of one sample. A maximum pressure of 1.6MPa was reached in 81.7 milliseconds.

In a comparative test two 16.51g samples of the uncoated pyrotechnic sheet generated a pressure of 1.4MPa in 103 milliseconds.

Claims

1. Pyrotechnic sheet material comprising a substrate of oxidizing material(11) and a coating layer of oxidizable material(12) on at least a portion of at least one surface of said substrate, the said substrate and said layer of oxidizable material being conjointly capable of reacting together exothermically on ignition; characterised in that
a layer of gas-generating deflagrating material(13) overlies at least a portion of the surface area of said substrate and/or said layer of oxidizable material, said deflagration material being ignitable by the burning of the said substrate and oxidizable material.

2. Pyrotechnic sheet material as claimed in claim 1, characterised in that said substrate is coated on both sides with oxidizable material and at least a portion of at least one of the layers of oxidizable material is covered with a layer of gas-generating deflagrating material.

3. Pyrotechnic sheet material as claimed in claim 1 or claim 2 characterised in that the gas-generating material comprises nitrocellulose-based propellant material, black powder, sodium azide/oxidizer composition or a potassium perchlorate/aluminium composition

4. Pyrotechnic sheet material as claimed in any one of claims 1 to 3 characterised in that the said layer of gas-generating material is from 3-100 microns thick.

5. Pyrotechnic sheet material as claimed in any one of claims 1 to 4, characterised in that said oxidizing substrate comprises polymeric film containing atoms chemically bound therein selected from the group consisting of halogens, oxygen, sulphur, nitrogen and phosphorous and the oxidizable material comprises metal selected from the group consisting of lithium, sodium, magnesium, beryllium, calcium,

strontium, barium, aluminium, titanium, zirconium and alloys thereof.

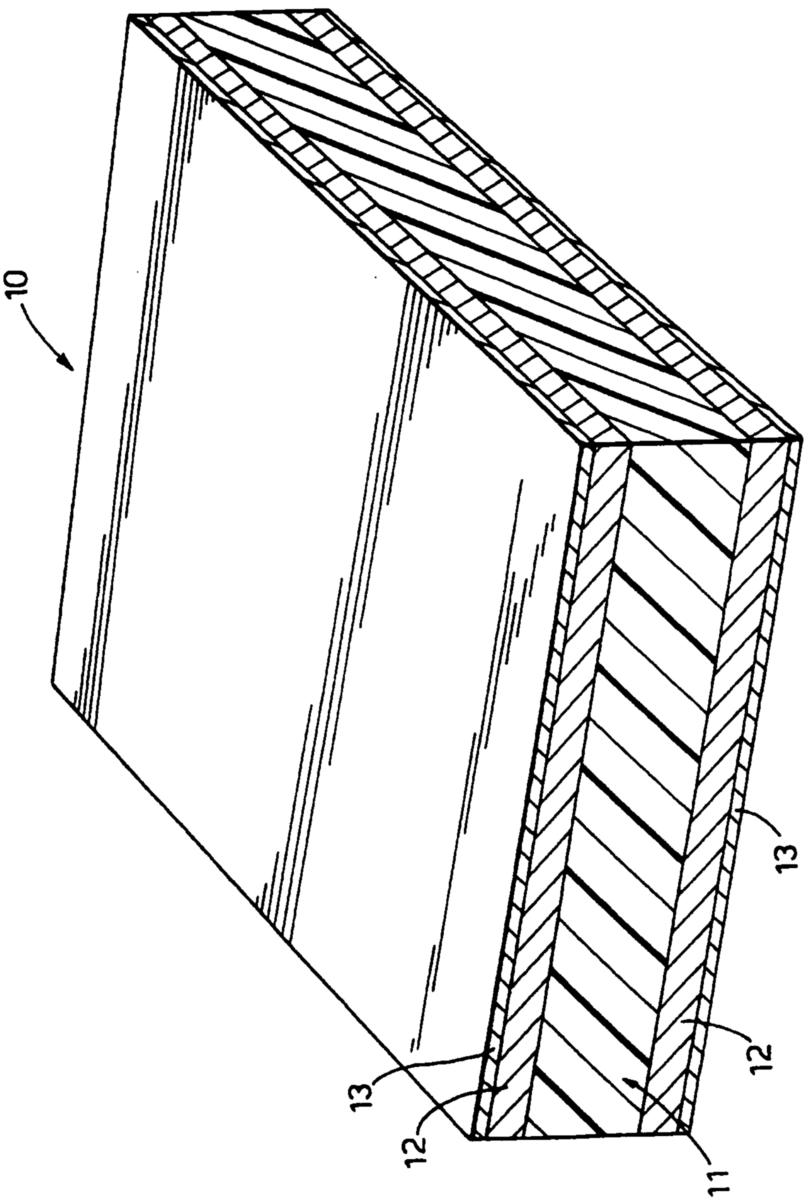
6. Pyrotechnic sheet material as claimed in claim 5, characterised the said polymeric film comprises interconnecting vapour-permeable pores having at least part of the oxidizable material vapour-deposited therein.

7. Pyrotechnic sheet material as claimed in any one of claims 1 to 6, characterised in that the oxidizing substrate and/or the layer of oxidizable material has discontinuous portions having flame-permeable apertures through which the interface between the oxidizing substrate and the oxidizable material is exposed.

8. A method of manufacturing pyrotechnic sheet material which comprises
depositing a layer of oxidizable material on at least a portion of at least one surface of a substrate of oxidizing material, said substrate and said oxidizable material being conjointly capable of reacting together exothermically on ignition; characterised in that an overlying layer of gas-generating deflagrating material is applied to at least a portion of the surface of the oxidizable material and/or the substrate in ignition transmission relationship with said substrate and oxidizable material.

9. A method as claimed in claim 8, characterised in that the gas-generating deflagrating material is applied as a solution or dispersion in a carrier liquid which is subsequently removed.

10. A method as claimed in claim 8, characterised in that the layer of gas-generating material is applied by corolling with the substrate and/or the layer of oxidizable material.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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 7127

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-3 213 793 (R.A. DRATZ) * column 3, line 24 - line 43; claims; figures 1,2 *	1-3,8-10	C06B45/14 C06C9/00
X	US-A-3 549 436 (A.V. LA ROCCA) * column 3, line 59 - line 72; figure 2 *	1-4,8,9	
A	GB-A-2 269 379 (IMPERIAL CHEMICAL INDUSTRIES PLC ET AL.) * claims; figure 1 *	1-10	
P,A D	EP-A-0 645 354 (IMPERIAL CHEMICAL INDUSTRIES PLC ET AL.) * claims; figures 1-10 * & GB-A-2 282 136	1-10	
A	GB-A-2 269 380 (IMPERIAL CHEMICAL INDUSATRIES PLC) * claims *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C06B
C06C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 February 1996	Schut, R

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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